

Biomorphic Ceramics from Lignocellulosic Templates

Mrityunjay Singh
Chief Scientist, Ohio Aerospace Institute
22800 Cedar Point Road
Cleveland, OH (USA)

President, The American Ceramic Society www.ceramics.org



Outline

- Introduction
- Anisotropy in Biological Systems in Nature
 - > Plants, Animals, Humans, etc.
- Wood as Engineering Material
 - > Anisotropic Properties
- Results and Discussion
 - > Thermal Conversion of Cellulose Templates
 - > SiC Based Ceramics from Cellulose Templates
 - > Templates for Carbon Nanotube Growth
 - > Biomaterials for Orthopedic Implants
- Summary and Conclusions



Why Look to Nature?



Termites build columns with heights that 2500 times their length

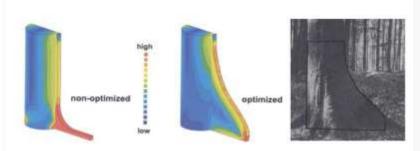


proportional thing, the structures would be 4600 meters tall (Prof. Turner's Book)



Natural Structures are Impressive The Tallest Tree, a REDWOOD, is 111 meters High. (EVAPORATIVE POSITIVE-DISPLACEMENT PUMP)

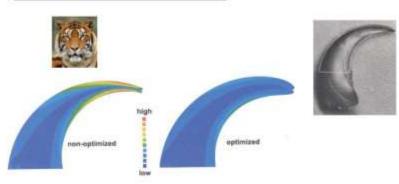
BENDING STRESSES IN A TREE TRUNK*



*C. Mattheck, Design in Nature: Learning from Trees, Springer, Berlin, p. 206.

Biological Systems in Nature are Optimized

STRESSES IN A TIGER CLAW*



*C. Mattheck, Design in Nature: Learning from Trees, Springer, Berlin, (1998) p. 186.



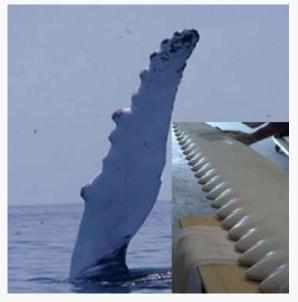
Nature Optimized Design Concepts for Commercial Products







Solar Biomimicry



Whale Biomimicry



Whale Flipper (Wind Power)

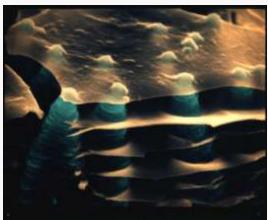
Tom Mueller, Biomimetics: Design by Nature, National Geographic, August 2008.



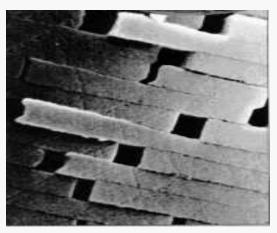
Strong, Lightweight Ceramics from Nature



Abalone Shell



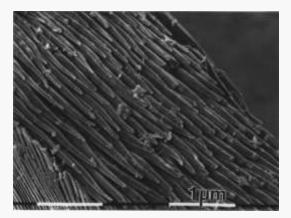
Growth Edge of Red Abalone



CaCO3 Laminated (Layered) Structure Provides Toughness



Rat's Tooth (Hydoxyapatite in Collagen Matrix)



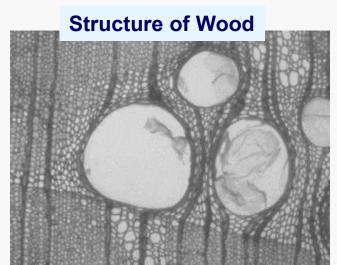
Sea-Urchin Teeth (CaCO3 calcite-fibers in CaCO3 matrix)



Shell of Bess Beetle (Fibrous Composite)



Many Biological Structures in Nature Are Porous With High Level of Ordering

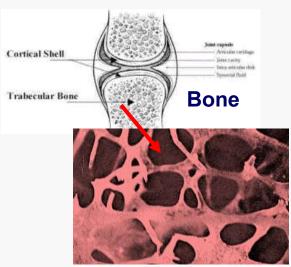


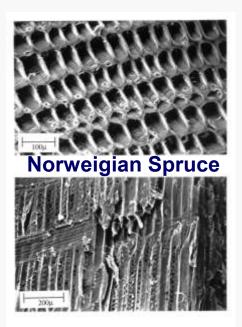
Structures Found in Nature Are Self-Assembled





Diatoms- self-assembled Silica based microorganisms





Some Features of Biological Systems:

- Porous, with pore sizes ranging from nanometers to microns
- Varying degree of ordering of the structure in three dimensions
- Self assembled
- Adaptive to different load situations
- Combination of structural and functional characteristics



Wooden Girder Bridges in Amsterdam



Bridge 102 (1795)



Todaiji Temple, NARA, Japan

(Largest Wooden Structure in the World)



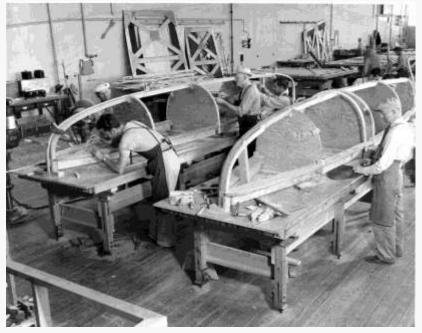




Howard Hughes Flying Boat "Spruce Goose"

(Biggest Aircraft Ever Built)



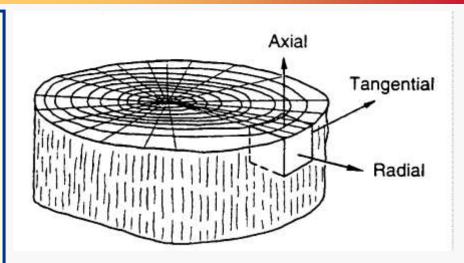


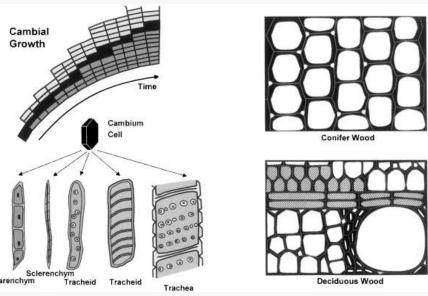
- Wingspan: 319.92'; Fuselage: 219'; Tailspan: 113.5'; Vertical Tailspan: 49.5'
- Gross Weight: ~ 400,000 pounds; Fuselage Height: ~ 30'
- Cruising Speed: ~ 200 mph



Microstructure and Anatomy of Wood

- Wood is a hierarchical cellular solid with relative density between 0.05 – 0.80.
- Composed of highly elongated cells (10-1000 aspect ratio) that make the bulk of the wood, rays (made up of smaller more rectangular cells) and sap channels.
- Softwoods: Cells relatively thin walled and interconnected by openings which allow fluid transfer.
 Rays are narrower and extend few cells in the axial direction.
- Hardwoods: Cells shorter, thicker walled, and provide strength. They also contain sap channels of much larger diameter. Rays extend hundreds of cells in the axial direction.

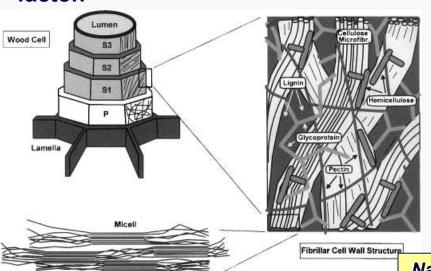






Anatomy and Composition of Wood

- Cell walls are made of fiber phase of crystalline cellulose in a matrix of amorphous hemicellulose and lignin ⇒ fiber reinforced composite.
- The lay-up of fibers in the wall is complex and critical for the strength and anisotropy. The cell walls are helically wound with the fiber direction nearer to the cell axis.
- The cell aspect ratio is another critical factor.



Cellulose Fibril

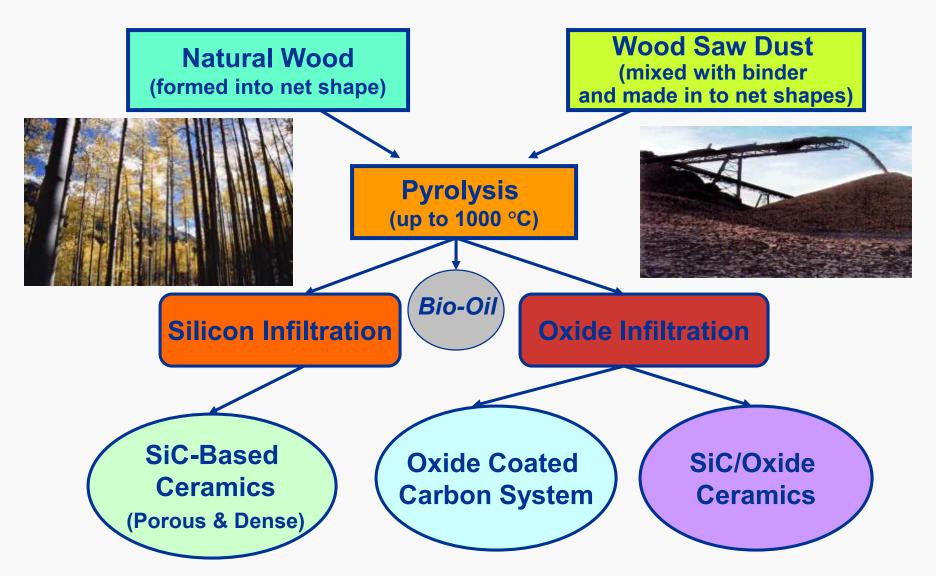
Natural tissues exhibit hierarchy, selectivity, and anisotropy combined in the cellular anatomy



Ecoceramics Technology



2001 R&D 100 Award, 2002 NorTech Innovation Award





Bio-Oil (Pyrolysis Liquid) Can be Used as Renewable Energy Source

Properties of Wood Derived Bio-Oil

Moisture content : 15-30%

• pH: 2.5

• Specific gravity: 1.2 (0.85 fuel oil)

• HHV as produced: 16-19 MJ/kg (Half of the conventional fuel oil)

Viscosity: 40-100 cp

• Solids (char): 0.5%

Elemental analysis: C (56.4%),
 H (6.2 %), O (37.3%), N (0.1%), Ash (0.1%)

Professor Tony Bridgwater Aston University, UK

Plant to Make BioOil From Wood and Other Types of Biomass



DynaMotive Technologies Corp. and Orenda Turbines, Canada

2.5 MW GT 2500 Turbine Generator



Advantages of Low Cost and Renewable Cellulosic Precursors for Ecoceramics

- Carbonization (Pyrolysis) of Natural Wood
 - Wood and carbon preforms can be fabricated in to near-net and complex shapes
 - No toxic gases generated during carbonization
 - Low cost
 - Multifunctional materials (anisotropic, FGMs)
- Preforms From Saw Dust From Timber Mills
 - Carbon preforms with saw dust as main component
 - Low cost, Isotropic materials

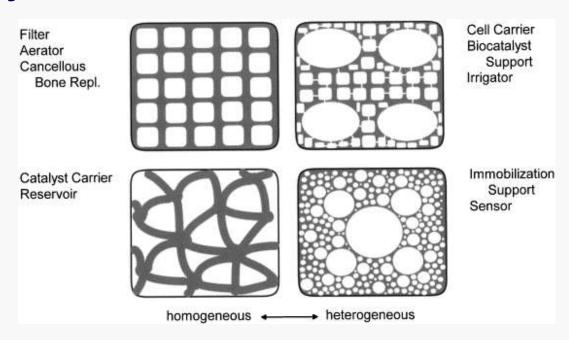
- Ecoceramics vs Traditional Ceramics
 - Use of Renewable Starting Materials
 - Utilization of Industrial Wastes (Conservation of Natural Resources)
 - No Toxic Pollutants Generated During Manufacturing
 - Lower Manufacturing Cost

Environmentally Conscious Green Manufacturing



Potential Applications of Ecoceramics Materials and Components

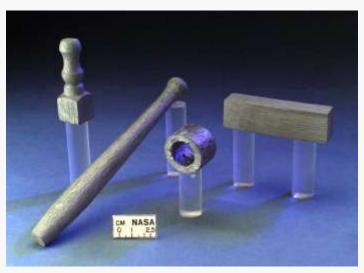
- Filters and catalyst support
- Automotive components
- Tooling and wear components
- Armor
- Lightweight, porous ceramics for aerospace systems



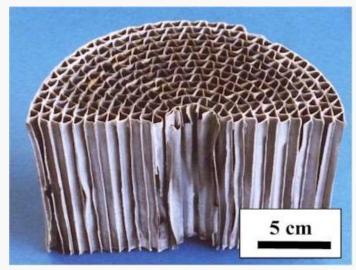


Complex Shaped Ecoceramics Components for a Wide Variety of Applications



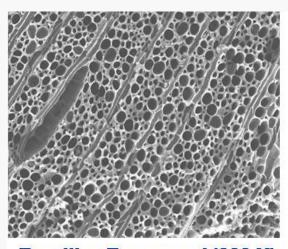




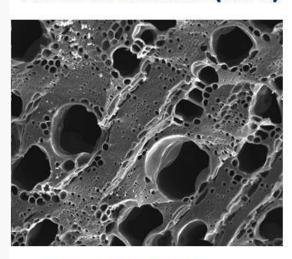




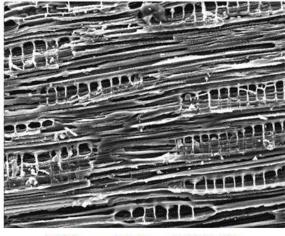
Carbonaceous Preform Microstructure Depends on the Microstructure of Wood



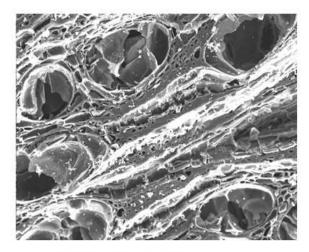
Brazilian Rosewood (300 X)



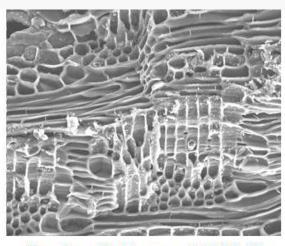
Pau Lope (200 X)



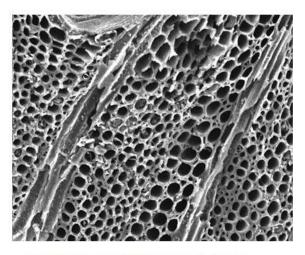
African Zebra (300 X)



Australian Jarrah (200 X)



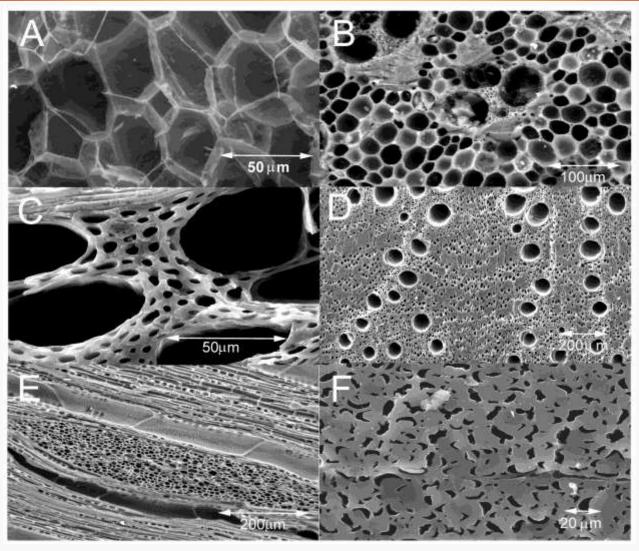
Ceylon Satinwood (300 X)



African Bubinga (100 X)



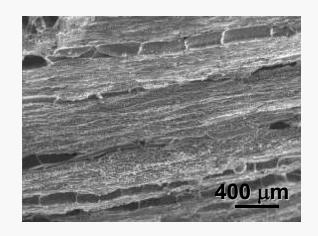
Carbonaceous Preform Microstructure Depends on the Microstructure of Wood

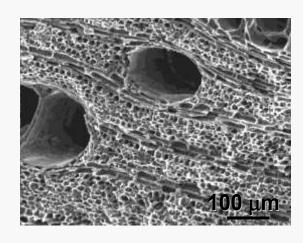


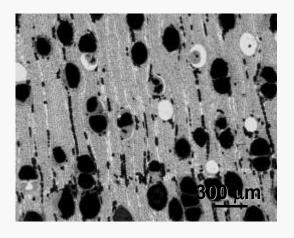
A) cork, B) bamboo, C) beech, D) Spanish oak (axial), E) Spanish oak (longitudinal), and F) red eucalyptus

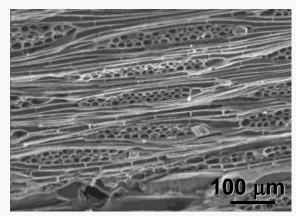


Microstructure of Porous Carbon Preforms and Silicon Carbide from Mahogany

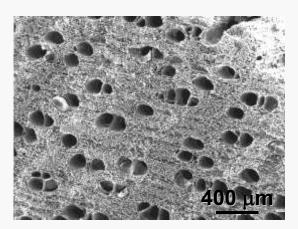




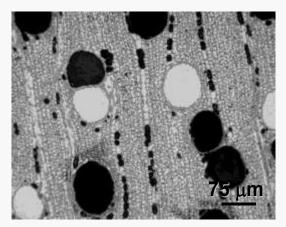




Parallel to Growth Direction



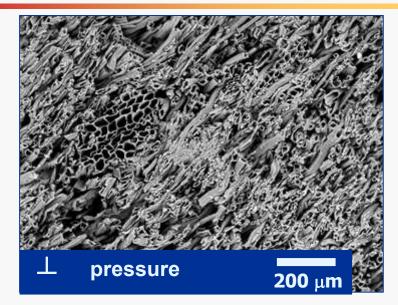
Perpendicular to Growth Direction

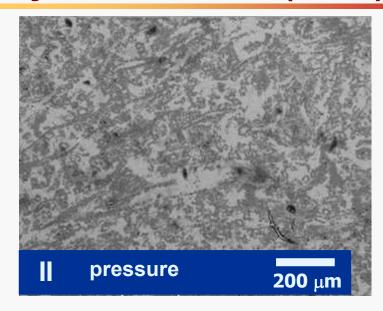


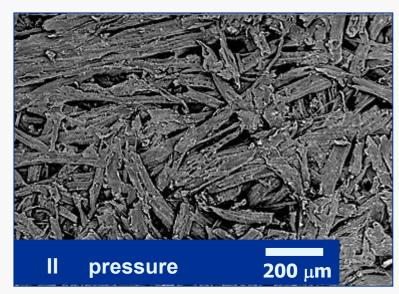
SiC Ceramics: Perpendicular to Growth Direction

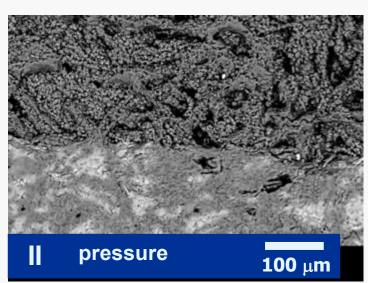


Biomorphic Silicon Carbide Ceramics from Medium Density Fiber Board (MDF)







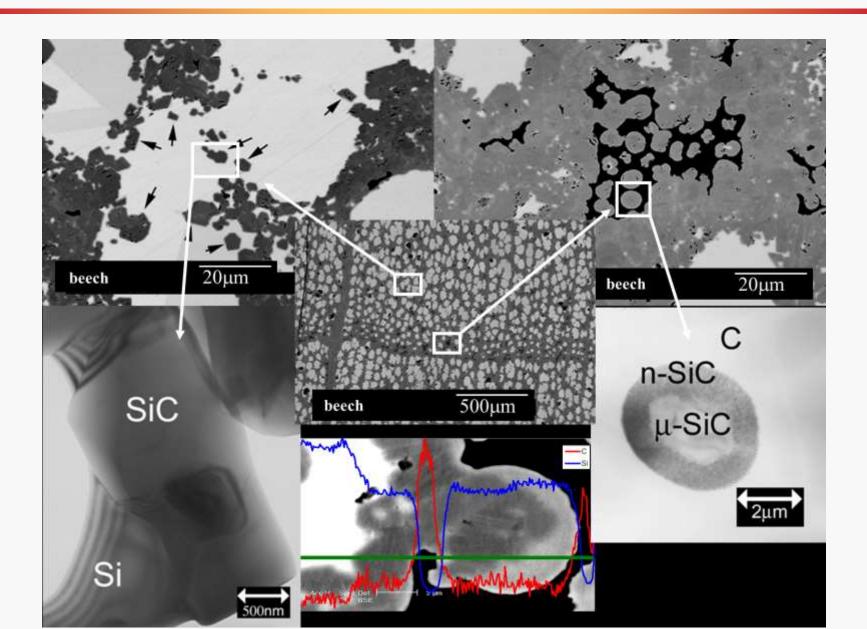


SiC/Si

Julian Martinez-Fernandez, University of Seville, Spain

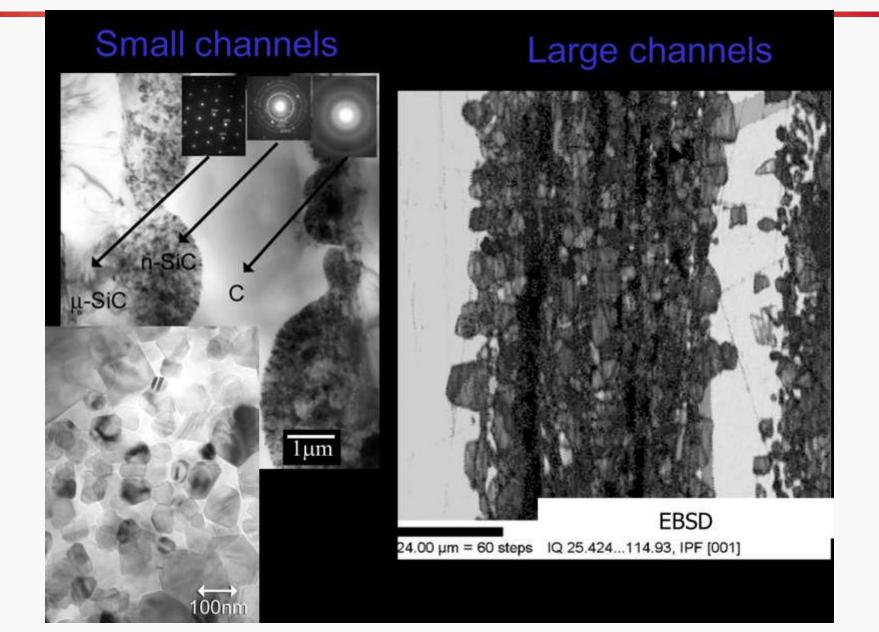


TEM Analysis of Biomorphic Silicon Carbide Microstructures



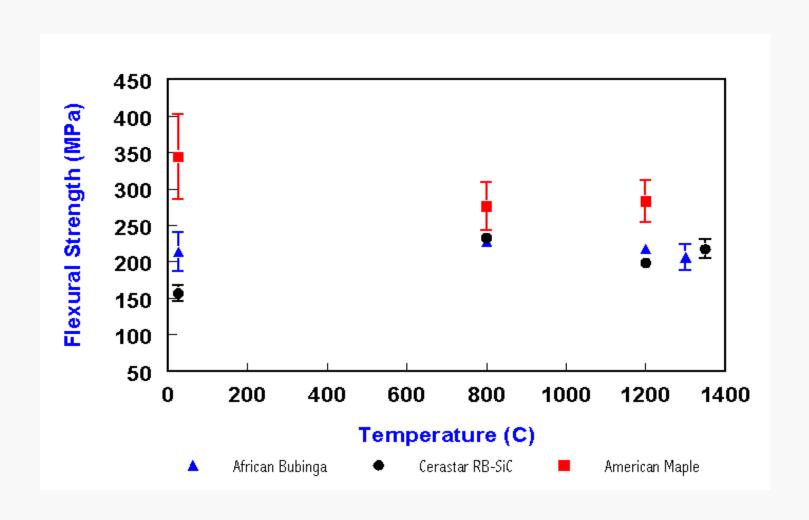


TEM Analysis of Biomorphic Silicon Carbide Microstructures



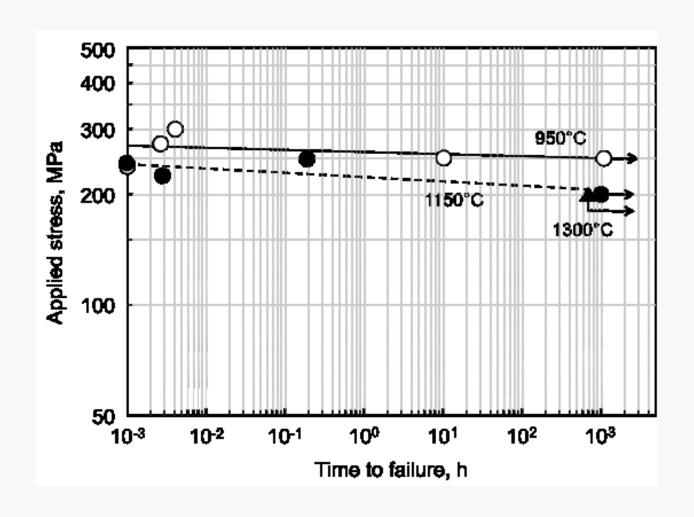


Mechanical Properties of Ecoceramics and Commercial RB-SiC at Different Temperatures



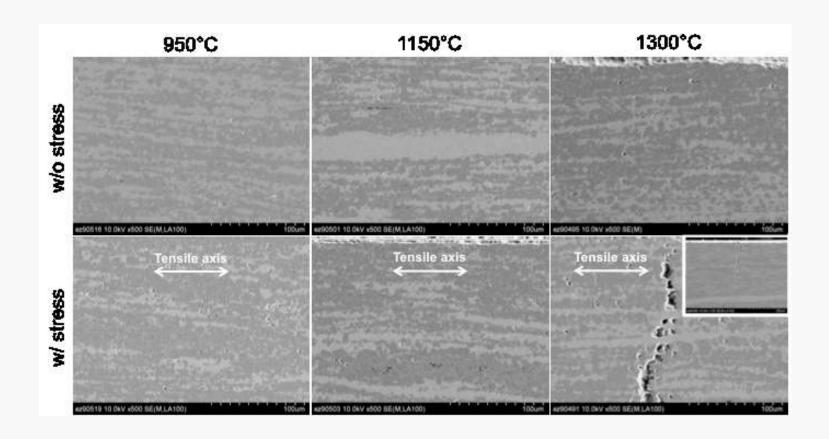


Time-to-Failure Behavior of Maple Derived SiC Ceramics from 950-1300°C in Air



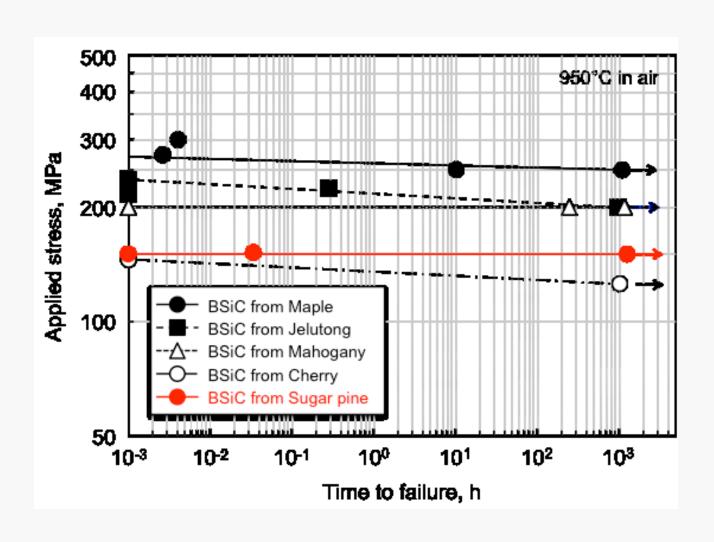


Post Test Evaluation of Maple Derived SiC Ceramics from 950-1300°C in Air



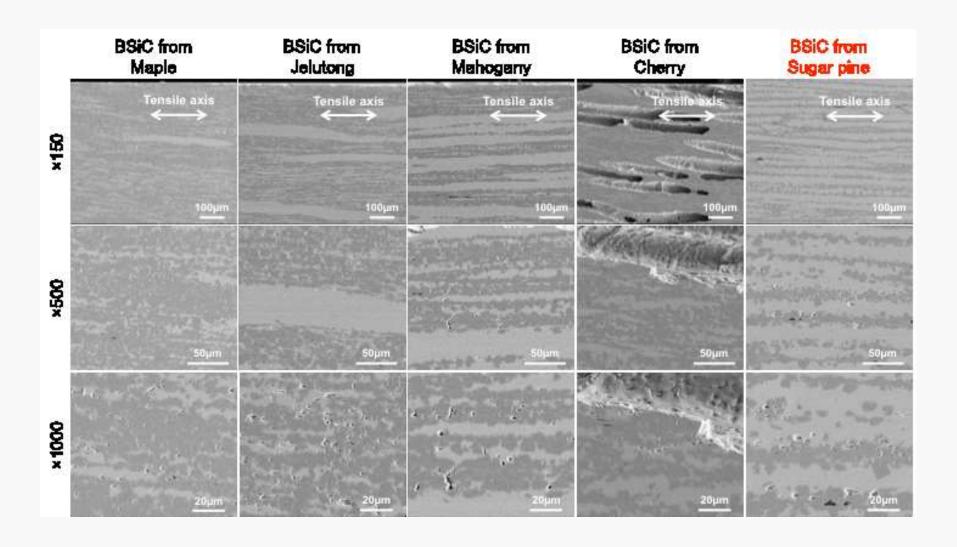


Time-to-Failure Behavior of Various Biomorphic SiC Materials at 950°C in Air





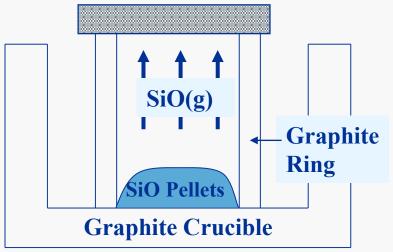
Longitudinal BSE Images of the BioSiC Materials after Testing over 1000h/950°C/Air

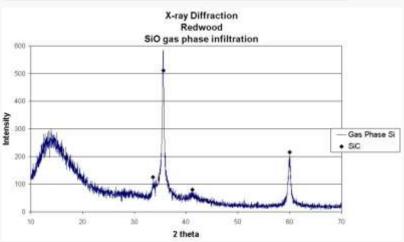


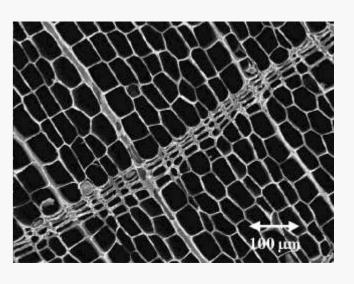


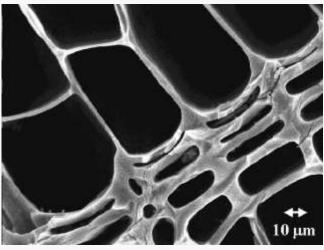
Templates for Growth of Nanotubes and Phase Change Materials (PCMs) for Energy Storage Devices

Carbon Preform



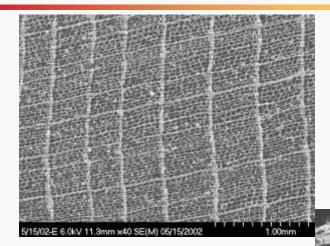




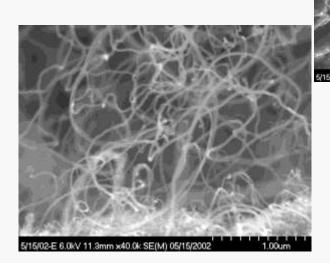


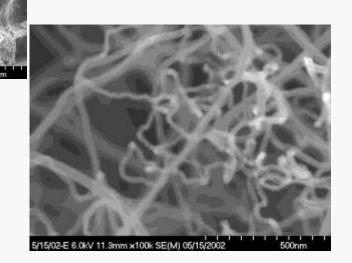


Growth of Carbon Nanotubes in Carbon Derived from Cellulose Templates (Redwood)



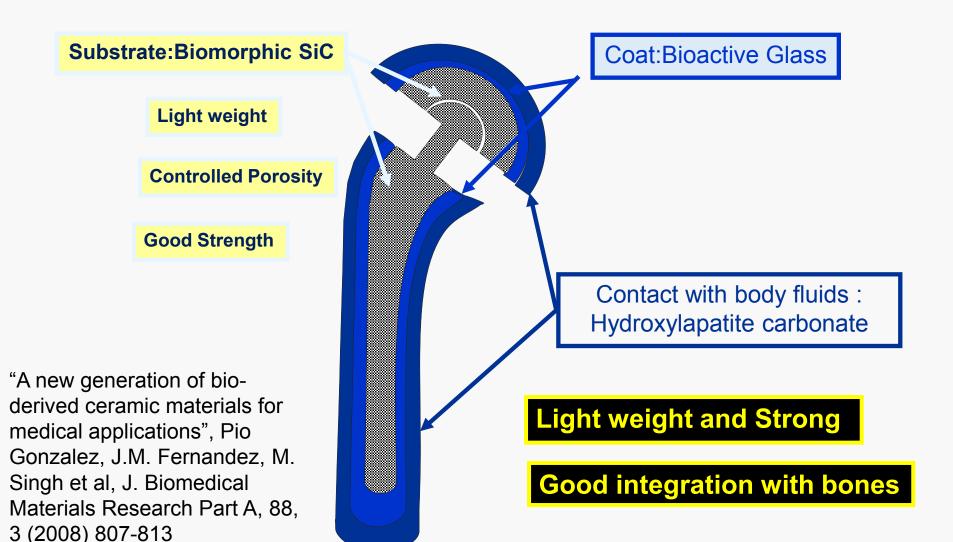








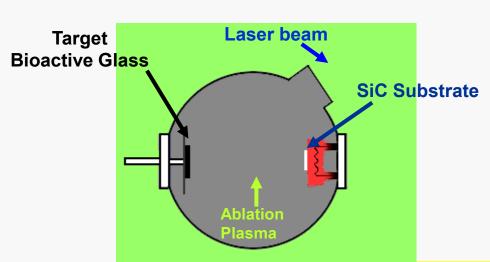
New Approach for Developing Biomaterials for Orthopedic Impaints

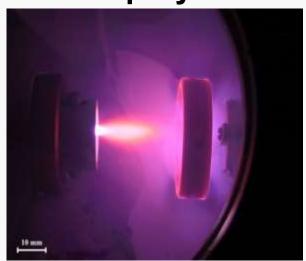


Fabrication of Coated Specimens

Pulse Laser Deposition (PLD)

Commercial Technique: Plasma Spray





>Low adhesion to substrates

- ➤ Deposition of high melting point materials
- ➤ Good adhesion between layers
- ➤ Stoichiometric composition
- ➤ No contamination



Implant Materials and Evaluation Methods

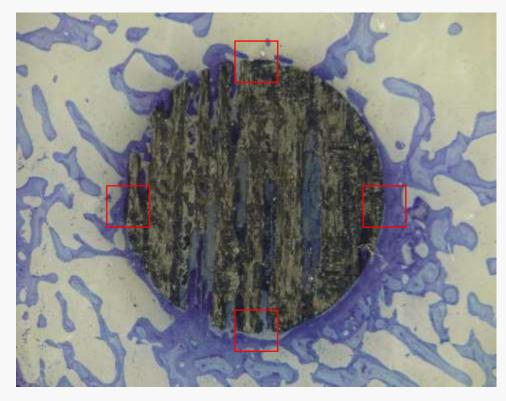
- Biomorphic SiC (bioSiC) and Titanium cylinders (4mm diameter,10mm length) were implanted in femur condyle of 15 rabbits.
- Twelve weeks later, specimens of 30 µm thick were studied by Optical Microscopy (OM), Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)



"Medical Devices Based on Bioinspired Ceramics", Pio Gonzalez, M. Singh, J.M. Fernandez in "Advances in Biomaterials" B. Basu et al. editor, Wiley (2009) pp 357-409.

PERIPHERICAL OSTEOINTEGRATION

- New bone formation around the implant
- No relevant inflamatory reaction and no fibrous tissue in the bone-implant boundary
- Bone density analysis at four cardinal points (1 mm²)

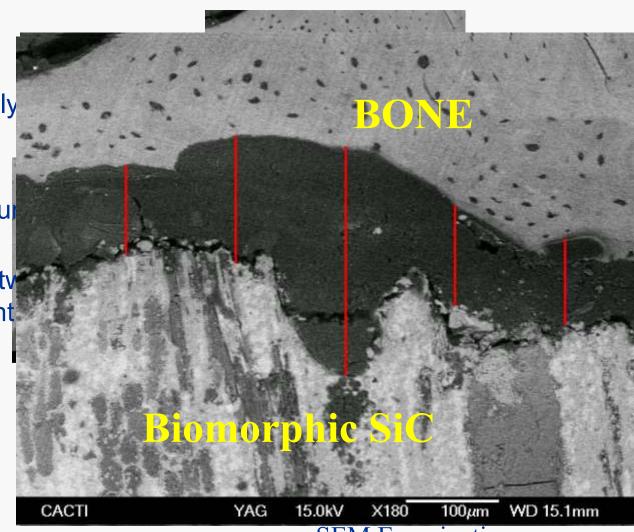


Histological examination

PERIPHERICAL OSTEOINTEGRATION

Detailed surface analy

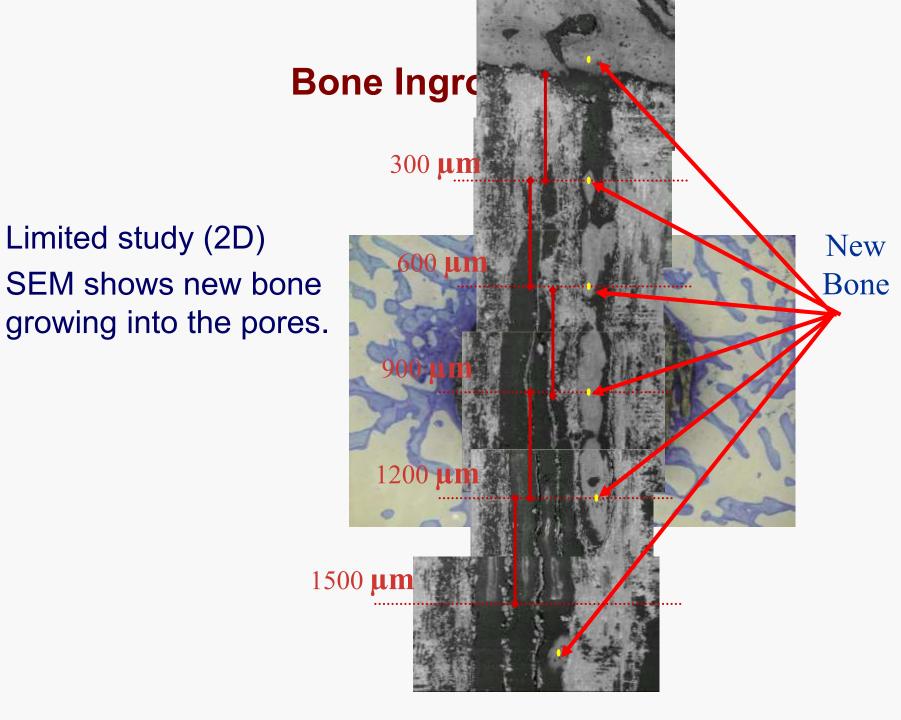
- Bonestmøtants arou intenface
 - manasuramentce between bone and SiC implant



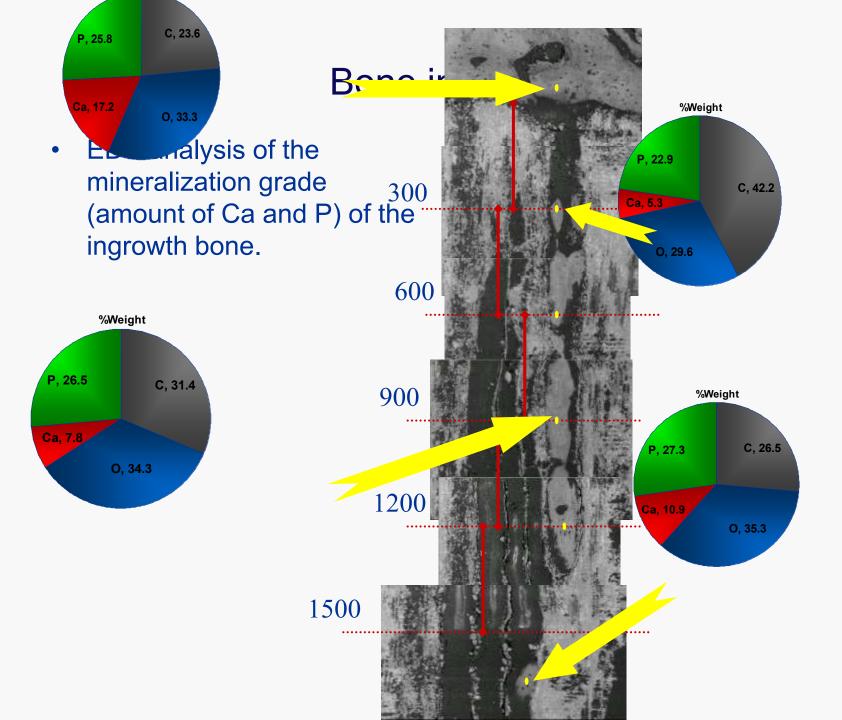


Bone-Implant Interface Thickness

	Bone-implant interface thickness (microns)					
Implant	1	2	3	4	5	Average
Pine-SiC	71,4	84,6	60,1	54,4	99,1	73,9
Sapeli-SiC	34,3	65,1	78,5	43,8	56,1	55,6
Titanium	35,1	11,7	27,0	33,8	50,6	26,6



Limited study (2D)





Summary and Conclusions

- Biological systems in nature can provide valuable information and guidance in design and manufacturing of new classes of materials.
- In the fabrication of biomorphic ceramics from cellulose templates, the original biostructure is retained throughout processing, which allows control of properties of the end products.



Acknowledgments

- Prof. J. Martinez-Fernandez, Dr. Joaquin Ramirez-Rico, and their group, University of Seville, Spain
- Prof. Pio González, University of Vigo, Spain
- Various colleagues and coworkers (Dr. Jon Salem, Ron Phillips, and many summer students over the years)
- Dr. Tadashi Matsunaga and Dr. H-T. Lin, Oak Ridge National Laboratory, TN